

# PATENT SPECIFICATION

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## DRAWINGS ATTACHED

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 WESTAWAY



## (54) SEPARATION OF METAL COMPOUNDS

(71) We, THE BRITISH PETROLEUM COMPANY LIMITED, of Britannic House, Moor Lane, London, E.C.2, a company incorporated in accordance with the Laws of England, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed to be particularly described in and by the following statement:—

This invention relates to methods of separating organometallic compounds from solutions in non aqueous solvents.

It is frequently desirable to separate organometallic compounds from organic liquids. A particular example of this is when such compounds are used as catalysts in homogeneous catalysts. In some cases the reaction product containing catalyst is thermally unstable so hot separation by methods such as distillation may be inapplicable. Furthermore organometallic compounds are frequently very expensive and recovery by a method that does not result in degradation is particularly desirable.

Our copending application No. 12173/68 serial No. 1,243,507 discloses a process for the separation of a transition metal complex from a homogeneous fluid mixture of the complex, which comprises bringing the mixture into contact with one side of a cellulosic membrane at an applied pressure greater than the pressure on the opposite side of the membrane, the pressure differential being greater than the osmotic pressure of the system.

Our copending application No. 51232/68 Serial No. 1,243,508 discloses a process for the separation of an organometallic compound from a solution of the compound in an organic component using a silicone rubber membrane and our copending application No. 30575/69 Serial No. 1260733 discloses a separation process using a polyolefin membrane.

We have now found that separation may be achieved by using a polyamide membrane.

Thus according to the present invention a process for the separation of an organometallic compound from a solution of the compound in an organic solvent comprises bringing the solu-

tion into contact with one side of a polyamide membrane at an applied pressure greater than the pressure on the opposite side of the membrane, the pressure differential being greater than the osmotic pressure of the system and the molecular cross section of the organometallic compound being greater than that of the organic compound and collecting the permeate the permeate having a reduced content of organometallic compound.

The invention also comprises a continuous process of homogeneous catalysis which comprises reacting a hydrocarbon and, optionally another organic compound, hydrogen, and carbon oxides in the presence of a co-ordination complex of a transition metal in which is produced a solution of the co-ordination complex in the liquid reaction mixture and separating the co-ordination complex from the reaction mixture as hereinbefore described.

The membrane can be external to the reaction zone, for example where the conditions of separation, for example temperature and/or pressure, differ from those of the reaction. Further, one or more separation steps other than membrane separation can exist between the reaction zone and a membrane separation step external to it.

By the term "organometallic compound" we mean those compounds which contain a metal and an organic moiety. The term is not limited to compounds containing a metal to carbon bond. The metal may be a transition metal e.g. nickel, rhodium or vanadium or a nontransition metal e.g. aluminium.

"Organic solvents" referred to hereinbefore means compounds containing carbon and hydrogen which may in addition contain any of oxygen, nitrogen, sulphur and phosphorus, for example, alcohols, aldehydes, ketones, organic acids amines and phosphines.

Typical organic solvents from which the organometallic compounds may be separated are heptaldehyde, toluene, benzene, xylene, n-hexane, n-heptane, butanol, isopropyl alcohol, butylamine thiopene etc. In general the polyamide membranes have been found to be more

permeable to non polar solvents e.g. hydrocarbons than polar solvents e.g. alcohols of comparable molecular weight and size.

5 The process for the present invention is particularly suitable for the separation of transition metal co-ordination complexes from their solutions in organic solvents for example the separation of rhodium complexes from the reaction mixture resulting from the hydro-

10 formulation of olefins.  
Thus the processes of the present invention can be employed in systems in which the organic compounds are alkenes having up to 20 carbon atoms per molecule and preferably 15 5 or less carbon atoms per molecule, in which hydrogen and/or carbon monoxide or carbon dioxide may be present and in which the transition metal complex contains one or more of metals of Groups VIII, VA and Group 20 VII A of the Periodic Table according to Mendeleef. The complex may also contain at least one biphyllic ligand and a bidentate ligand co-ordinating through at least one oxygen atom. Thus for example, a suitable mixture 25 comprises the reaction product of the hydroformulation of a lower olefin in the presence of carbon monoxide and hydrogen, a typical catalyst is a rhodium complex in which the biphyllic moiety is tri *n*-butyl phosphine and the bidentate moiety is acetylacetonate i.e.  $\text{Rh}(\text{Bu}_3\text{P})\text{Co}(\text{acac})$ . The products from this reaction are alcohols and/or aldehydes, depending on the catalyst concentration, and the reaction is further discussed in our copending 30 U.K. Patent Application No. 55295/67. Serial No. 1,243,189. Another suitable system is that in which a lower olefin is dimerised in the presence of a nickel acetylacetonate complex promoted by aluminium diethylethoxide.

40 Other typical rhodium complexes which can be separated from solution in organic components are  $\text{Rh}(\text{Bu}_3\text{P})_2\text{CO Propionate}$ ,  $\text{Rh}(\text{Et}_3\text{P})_2\text{COCl}$ ,  $\text{Rh}(\text{iPr}_3\text{P})_2\text{COCl}$  and  $\text{Rh}(\text{Bu}_3\text{P})_2\text{COCl}$  where *iPr* is an isopropyl and Bu a *n*-butyl radical.

45 The membranes may also be used to separate nickel and vanadium containing complexes for example the porphyrins for example etioporphyrins from hydrocarbon solvents such as toluene.

50 Preferred polyamides are those of M.W. from 10,000 to 30,000. The polyamides may be prepared by methods known in the art for example as described in U.S. Patents 2,130,523; 2,130,947; 2,130,948; 2,071,253 and U.K. Patents 461,236; 461,237 and 474,999.

55 The polyamide membrane should be insoluble in the organic component of the mixture to be separated.

60 The membrane may be prepared from the polyamide by the methods described for polyolefins in our copending application No. 30575/69 Serial No. 1260733.

65 The thickness of the membrane is as low as

possible consistent with the membrane having sufficient strength to withstand the applied pressure. Preferably the thickness is in the range  $0.1\mu$  to  $25\mu$ .

The membrane can, but need not necessarily be in the form of a disc. It should be in a form suitable to withstand the operating conditions to which it is subjected, particularly elevated pressure. To obtain a high output the maximum possible surface area of the membrane that can be achieved should be exposed to the components to be separated. Before use the membrane is preferably pretreated by soaking in the feedstock to be separated.

Operating conditions in the processes of the invention will depend mainly on the nature and method of conditioning of the membrane and also on the components to be separated. The main operating variables, however, are pressure, temperature and complex concentration. Separation is believed to arise because small organic components can diffuse through the labyrinth structure of polyamide membranes more readily than the bulky and possibly more rigid organometallic compounds. Accordingly the best separations are achieved when the organometallic compound is large and bulky compared to the organic component. Thus the minimum cross section of the molecule of the organometallic compound should be greater than that of the organic compound and should desirably be greater than  $8\text{\AA}$ . The large the difference in size than the better is the separation, desirably the cross section of the organometallic compound is at least 50% greater than that of the organic components. Preferably, also the molecule of the organometallic compound is more rigid than that of the organic compound.

The applied pressure may be in the range from just greater than the osmotic pressure of the system to about  $30,000\text{ kNm}^{-2}$ . Suitably the applied pressure is in the range 500 to  $20,000\text{ kNm}^{-2}$  preferably 3000 to  $20,000\text{ kNm}^{-2}$ .

Suitable operating temperatures are in the range 0 to  $150^\circ\text{C}$ . Preferred temperatures are in the range 20 to  $100^\circ\text{C}$ . The concentration of the organometallic compound may be very low e.g. about 1 p.p.m. especially when used as a homogeneous catalyst or fairly high e.g. 10% by wt. A typical upper limit is about 5% by wt. Preferably the concentration is in the range 1 to 1000 parts per million by wt.

In the separation of rhodium complexes from hydroformylation products, temperatures up to about  $150^\circ\text{C}$  and concentrations up to 1% by wt. are preferred.

The present invention is illustrated with reference to the flow system and apparatus described in the accompanying drawings, in which;

Figure 1 shows schematically the high pres-

sure flow system used, and

In figure 2 a stainless steel high pressure cell is shown. In Figure 1 feedstock was supplied from a reservoir 1 at atmospheric pressure, to which dry nitrogen could be supplied if necessary via line 8. The feedstock was pressurised by means of a hydraulic diaphragm pump 2 and supplied to the cell 3. Permeated material left the cell to collection via line 4. Non-permeated material returned to the reservoir 1 via a felt filter 5 and a pressure control valve 6. A cell by-pass line 7 was provided containing a pressure relief valve 9 operating at 3000 psig. Pressures were read from gauge 10.

In Figure 2 a membrane 11 7.8cms in diameter (permeable area 23 cm<sup>2</sup>) is cushioned by filter paper 18 and is supported on a sintered stainless steel disc 12 (of 6 $\mu$  pore size) resting in a circular recess 19 in the cell base 13. Gramophone grooves 20 cut into the bottom of the recess facilitate permeable drainage 17. Six allen capped screws 21 secure the cell top 14 and base 13 together, thereby sealing the membrane 11 against a nitrile or teflon 'O' ring 15 carried in the cell top 14. An outer 'O' ring prevents permeate linking to the outer edge of the sintered disc 12 and returning into the feed. To create turbulence in the cell, feedstock enters through a 1 mm orifice

16. The dead volume of the cell is 3.5 mls.

The flow system and apparatus described were used to investigate the separation of a catalyst complex from its reaction mixture, and conditions and the results obtained are given in the following Example. In these investigations rates of permeation (PR) were determined by measuring the volume of permeate collected over known periods of time. The metal contents of the permeates and feedstocks were measured by X-ray emission so that the resistance of the membrane to catalyst to catalyst permeation could be expressed in terms of solute retention (SR), where SR was the ratio, expressed as a percentage, of the difference between the metal content of the feedstock and the permeate to the metal content of the feedstock.

The invention is illustrated in the following Example.

#### EXAMPLE 1

Using the apparatus illustrated in Fig 1 and 2, polyamide membranes were used to separate a rhodium complex of formula Rh(Bu<sub>3</sub>P) CO (acac) where acac is acetylacetonate from solution in toluene. The concentration of complex was 80 p.p.m.

The results are summarised in the following Table.

| Membrane                     | Pressure (kNm <sup>-2</sup> ) | Permeation Rate (lh <sup>-1</sup> m <sup>-2</sup> ) | % Rh complex retention |
|------------------------------|-------------------------------|---|------------------------|
| 1                            | 3450                          | 3.9   | —                      |
| Membrane thickness 0.5 $\mu$ | 6900                          | 4.8   | 87.0                   |
| 2                            | 3450                          | 1.8   | 92.0                   |
| Membrane thickness 0.5 $\mu$ |                               |   |                        |

Membrane 1, was prepared from Grilamid L25 ex Emser Werke which is a nylon 12 prepared from 12 aminododecanoic acid. Membrane 2 was prepared from isophthalic acid (mole ratio 60) terephthalic acid (40) hexamethylene diamine (85) and iso-phorone diamine (15). The membranes were prepared at room temperature by casting from a solution in a 50/50 w/w blend of chlorobenzene and m-cresol. The concentration of the solution was 1 to 2%. Glass slides were immersed in the solution at 25°C, allowed to stand for about 1 hour and then withdrawn at the rate of about 2 cms per second. The membranes were formed on the glass slides by allowing the solvent to evaporate at room temperature and removed from the slides by immersing in cold water and floating the film from the glass. The membranes were removed from the water

surface by floating onto Gelman Metrical Filter, 0.1 $\mu$  pore size.

The membranes were then dried or used directly in an ultrafiltration cell in which the membrane and filter are supported on a sintered stainless steel disc.

The Grilamid polyamide L.25 was a nylon 12 extrusion grade, having an intrinsic viscosity ( $\eta$ ) = 1.46 in conc H<sub>2</sub>SO<sub>4</sub> 0.15% (w/v) at 25°C; a number average molecular weight  $M_n$  = 19,840/Osmometry, m-cresol/chlorobenzene (1:1) at 35°C). The polyamide used for membrane 2 was prepared as described in Netherlands Patent Application 6806792 and had the following properties: intrinsic viscosity ( $\eta$ )<sub>1</sub> = 0.99 in conc H<sub>2</sub>SO<sub>4</sub> 0.15% (W/V), number average molecular weight  $M_n$  = 13,500 (Osmometry, m-cresol/chlorobenzene (1:1) at 35°C).

## WHAT WE CLAIM IS:—

1. A process for the separation of an organometallic compound from a solution of the compound in an organic solvent which  
5 method comprises bringing the solution into contact with one side of a polyamide membrane at an applied pressure greater than the pressure on the opposite side of the membrane, the pressure differential being  
10 greater than the osmotic pressure of the system and the molecular cross section of the organometallic compound being greater than that of the solvent and collecting the permeate, the permeate have a reduced content of the  
15 organometallic compound.
2. A process as claimed in claim 1 wherein a solution of a co-ordination complex of a transition in a reaction product mixture resulting from the hydroformylation of olefins is  
20 contacted with the membrane.
3. A process as claimed in claim 2 wherein the transition metal is rhodium.
4. A process as claimed in any one of claims 1 to 3 wherein the polyamide has a  
25 molecular weight of from 10,000 to 30,000.
5. A process as claimed in any one of claims 1 to 4 wherein the thickness of the polyamide membrane is in the range 0.1 to 25 microns.
6. A process as claimed in any one of claims 1 to 5 wherein the pressure is in the range 500 to 20,000 kN per sq. metre gauge.
7. A process as claimed in any one of claims 1 to 6 wherein the temperature is in the range 0 to 150°C.
8. A process as claimed in any one of claims 1 to 7 wherein the concentration of the compound is within the range 1 to 1000 parts per million by weight.
9. A process for the separation of organometallic compounds substantially as hereinbefore described with reference to the Example.
10. Organometallic compounds whenever separated by a process as claimed in any of claims 1 to 9.
11. A continuous process involving homogeneous catalysis which comprises reacting a hydrocarbon in the presence of a co-ordination complex of a transition metal in which a solution of the complex in the liquid reaction product mixture is formed and separating the co-ordination complex from the reaction mixture by a process as claimed in any one of claims 1 to 9.

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FIG.1.

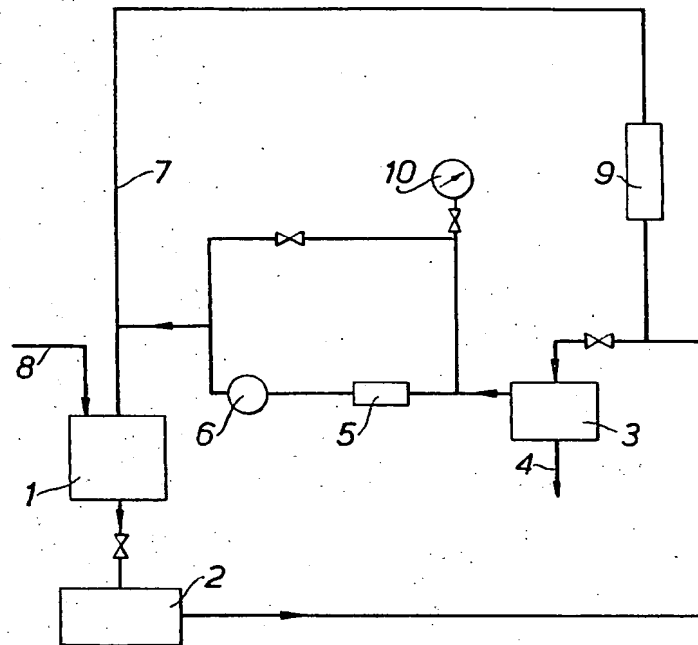
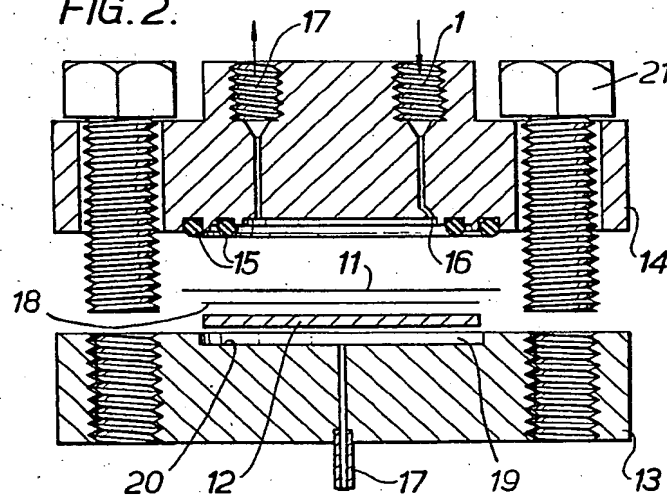


FIG.2.



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